Identification of Position Isomers of Some Stearic Acid Derivatives by Infrared Spectroscopy

Study of *trans* 6- through 11-Octadecenoic Acids and Corresponding Contiguously Substituted Dihydroxystearic Acids in the Crystalline State

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▶ The position of the double bond in *trans* 6- through 11-octadecenoic acids can be determined by studying the equally spaced absorption bands in the 1180- to 1350-cm.$^{-1}$ region. This band progression, which in the case of *n*-saturated fatty acids depends on the total chain length, is related to the chain segment next to the carboxyl group. The corresponding dihydroxy acids can be distinguished by studying the 800- to 1200-cm.$^{-1}$ region. The high and low- melting series show distinct differences. Spectral variations within the low- or high-melting series are small, but in many cases sufficient to permit positive identification.

Jones, McKay, and Sinclair have pointed out that in the infrared absorption spectra of crystalline fatty acids a progression of uniformly spaced bands is observed in the 1180- to 1350-cm.$^{-1}$ region and that the number of bands in the progression is related to chain length (*4*). For *cis*-unsaturated acids the progression becomes irregular, but for *trans*-9,10-octadecenoic acid, the region is similar to one of the short chain saturated acids—e.g., lauric—suggesting independent behavior of the two chain sections (*4*). Corish and Chapman (*2*) found similar bands in the spectra of lower homologs (C_2 to C_{12}), although the regularity seems to decrease with decreasing chain length. Meiklejohn *et al.* (*6*) have found that in the higher members the number of bands in the progression is approximately equal to half the number of carbons in the chain. Jones, McKay and Sinclair (*4*) suggested that the bands arise from the rocking and/or twisting vibrations of the CH_2 groups. Ferguson (*3*) noticed that the single crystal spectra of eicosanoic acid obtained with polarized radiation by Cole and Jones (*1*) do not show parallel polarization of the progression bands, as would be expected for wagging or twisting modes. Meyer and Schuette (*7*), who studied over 300 long-chain compounds, observed that all isomeric cis and trans forms of the octadecenoic acids gave fewer bands in the 1180- to 1850-cm.$^{-1}$ region than was observed

for stearic acid. As the double bond approached the terminal methyl group, these bands increased in number.

Five position isomers of *trans*-octadecenoic acid have been examined for correlations between the band progression and the position of the double bond. The results indicate that the number of bands in the progression series is related to the (total) length of the chain segment next to the carboxyl group. This offers a way to determine the location of the double bond in *trans*-monounsaturated fatty acids. In the particular series studied, the results are unambiguous. One sample (elaidic acid) was studied with polarized radiation to pinpoint the progression bands and locate the 1300-cm.$^{-1}$ region carboxyl band. The results indicate that the weak bands on the high frequency side of the progression region are of a different nature than the four main bands and that—contrary to saturated acids and particularly, eicosanoic acid (*1*)—no distinct carboxyl band is found in this region.

Experimental. The fatty acids have been described (*9*). The infra-

red spectra were obtained using a Beckman Model IR-3 instrument equipped with sodium chloride optics and a Perkin-Elmer Model 21 instrument equipped with sodium chloride optics and a silver chloride polarizer. The latter was used to study the sample of trans-9,10-octadecenoic acid with polarized radiation. trans-6,7-; trans-7,8-; trans-8,9-; trans-9,10-, and trans-11,12-octadecenoic acids were studied as potassium bromide pellets. These were prepared by grinding about 1.5 mg. of the dry solid sample together with about 300 mg. of dry potassium bromide for 2 minutes in a vibrator-grinder and pressing the resulting mixture in a $^1/_2$-inch diameter die by applying a total force of 20,000 pounds for 5 minutes.
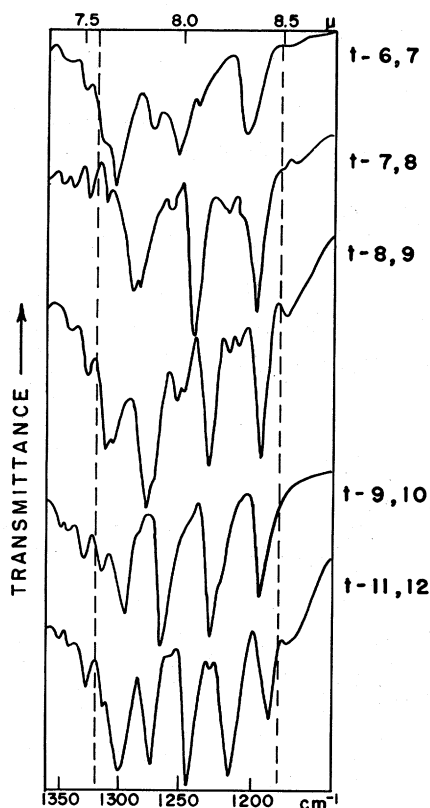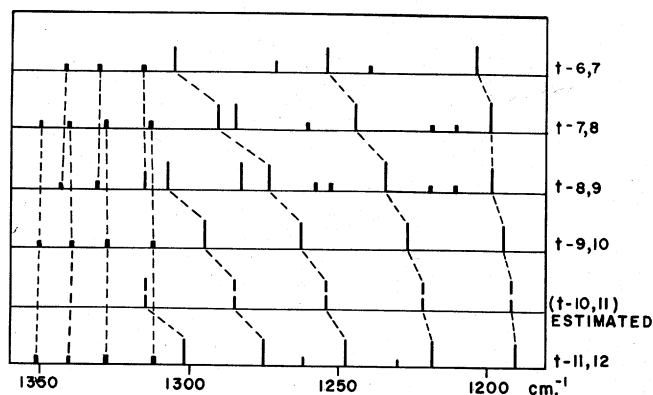
An oriented sample of the trans-9,10-acid was prepared by melting the substance between two rock salt plates and subsequent cooling, using a temperature gradient. The resulting oriented film was studied with the electric vector first parallel and then perpendicular to the direction of crystal growth.

Results and Discussion. Figures 1 and 2 illustrate that in the region roughly between 1180 and 1320 cm.$^{-1}$ there exists a series of relatively strong, equally spaced bands just as in the case of saturated acids. The "rule of two" relationship observed by Meiklejohn and coworkers (6) apparently applies to the first segment of the hydrocarbon chains in the trans-unsaturated acids studied. The number of these bands is equal to $n/2$ for the even members and to $(n-1)/2$ for the odd members, if n is the number of carbon atoms in the chain segment between the carboxyl group and the double bond, the end atoms of the segment included. Some weaker, irregular bands are also observed, but the regular spacing and higher relative intensity of the progression bands makes their recognition relatively easy. Although in the saturated fatty acids the number of bands is indicative of the whole chain length, in unsaturated acids, the bands indicate the length of the chain segment next to the carboxyl group. This is illustrated by a comparison of Figures 2 and 3. Figure 3 shows schematically the approximate positions and relative intensities of the progression bands of the C_6 to C_{12} saturated acids. The data are computed from absorption curves published recently by Corish and Chapman (2) and obtained by them on solid samples using a low temperature cell. Data for the C_{11} saturated acid and trans-10,11-octadecenoic acid were not available.

The estimated band positions for these compounds are indicated by broken lines in Figures 2 and 3.

On the high frequency side of the band progression of the unsaturated acids there exists another progression of much weaker intensity (Figures 1 and 2). These bands are not influenced by the position of the double bond and appear at about the same positions for all odd and even acids studied. They should not be included in the progression which is related to the length of the chain segments.

The terminal chain segments (from the double bond to the methyl group) do not seem to give rise to regularly spaced medium intensity bands. In this aspect they behave much like unsubstituted n-paraffins which show progression bands of considerably lower intensity and less regular spacings than the corresponding fatty acids. Some weak bands occurring between the main progression bands, and partially overlapping with them, might be caused by the terminal segments, but no conclusions seem possible at present, except that the double bond effectively interrupts the chains without having a noticeable activating effect.

Complications may be encountered in determinations of the lengths of chain segments by the band progression method of which the first is the problem of polymorphism. Jones, McKay, and Sinclair (4) have shown that in the case of stearic acid, various polymorphic forms absorb differently in the infrared, including the progression region. In the case of trans-octadecenoic acids, no polymorphism has been reported (5). No irregularities which might be caused by different crystal configurations have been found in this laboratory. Nevertheless, polymorphism is a potential source of trouble and should
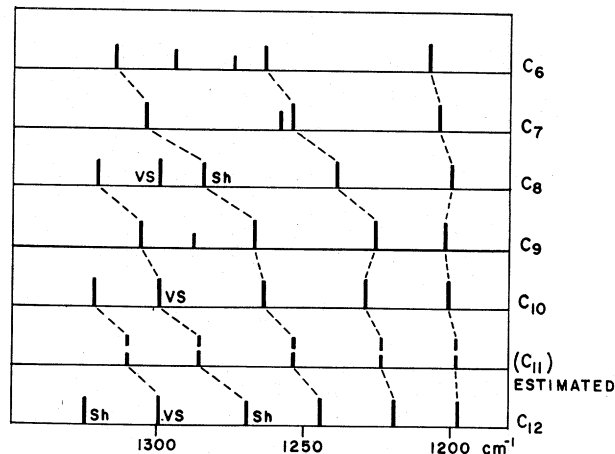
Figure 1. 1175- to 1350-cm.$^{-1}$ region of trans-octadecenoic acids

Figure 2. Schematic presentation of absorption bands of trans-octadecenoic acids in 1175- to 1350-cm.$^{-1}$ region

Figure 3. Schematic presentation of absorption bands of C_6 to C_{12} saturated fatty acids in 1175- to 1350-cm.$^{-1}$ region
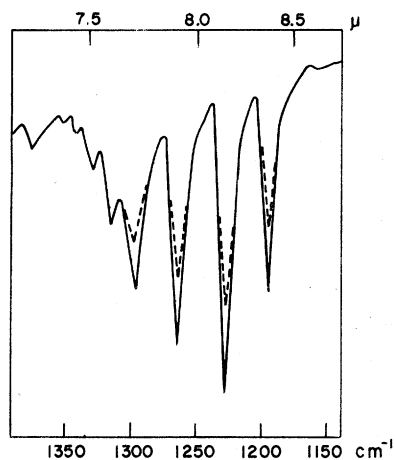
VS. Very strong   SH. Shoulder

Figure 4. 1150- to 1350-cm.$^{-1}$ region of *trans*-9,10-octadecenoic acid observed with polarized radiation

— Electric vector parallel to direction of crystal growth
--- Electric vector perpendicular to direction of crystal growth

Figure 5. 1550- to 700-cm.$^{-1}$ region of high and low melting 6,7-, 8,9-, 9,10-, 11,12-dihydroxystearic acids

be considered in attacking a new group of compounds.

Also, in most fatty acid spectra there is a strong carboxyl band around 1300 cm.$^{-1}$ which overlaps with the progression and sometimes renders the counting of the significant bands difficult. Figure 3 shows the presence of such a band in several of the saturated acids. In the series of octadecenoic acids no band which could obviously be assigned to the carboxyl group was found. Cole and Jones (1) have shown that in eicosanoic acid, the 1300-cm.$^{-1}$ carboxyl band is polarized differently from the progression bands. In *trans*-9,10-octadecenoic acid, on the other hand, all four major bands in the progression region show the same polarization, whereas the weak bands on the high frequency side of the region show no polarization under the same conditions (Figure 4). This seems to indicate that the carboxyl band is relatively weak in this series and does not overlap with the bands of the progression.

A further problem is the setting of the frequency limits of the progression region. For the saturated acids, Meiklejohn et al. (6) have somewhat arbitrarily chosen the region between 7.43 and 8.47 microns (about 1346 to 1180 cm.$^{-1}$). This is not appropriate in this series of unsaturated compounds. The weak bands in the 1300- to 1350-cm.$^{-1}$ region should be excluded because the spacings are irregular, the positions do not change with chain length, the intensity is considerably lower, and the polarization characteristics are different. These observations indicate that no universally valid progression region can be defined.
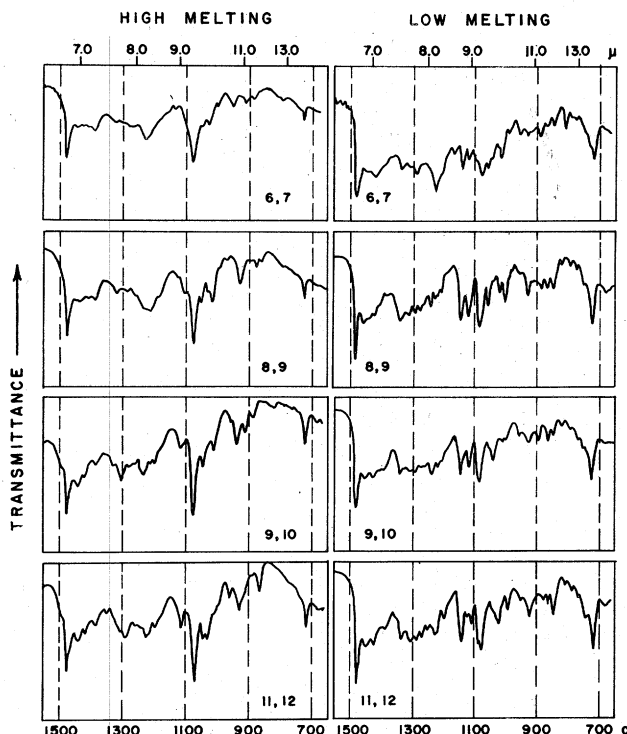
For each group of compounds the bands belonging to the progression should be identified separately by applying the above criteria.

Progression bands are usually assigned to coupled —CH$_2$— wagging and/or twisting vibrations (4, 6). Ferguson (3) has recently pointed out that for eicosanoic acid the polarization data (1) are not in agreement with such an assignment. The results obtained by Meiklejohn et al. (6) on saturated acids and obtained in this laboratory on the octadecenoic acids indicate that the number of bands is closely related to the total length of the chain (or chain segment) rather than the number of CH$_2$ units. The same conclusion is suggested by the data of Corish and Chapman (2).

DISTINGUISHING BETWEEN POSITION ISOMERS OF CONTIGUOUSLY SUBSTITUTED DIHYDROXYSTEARIC ACID

Hydroxylation results in a different kind of modification of the basic structure than unsaturation. The chain of single-bonded carbon atoms is preserved, but the regular packing of the individual molecules is altered by the voluminous hydroxyl groups as well as by the new hydrogen bonds introduced. A different type of change in the band progression, which depends on the packing of the molecules as well as on the length of chain segments (8) would be expected. Specific COH absorption bands should occur around 3400 and 1000 cm.$^{-1}$ The exact positions of these bands would be expected to depend on the position of the hy-

droxyl groups and on the hydrogen bonds formed.

Experimental. The preparation of the high and low melting dihydroxy stearic acids has been described (9)- Infrared spectra of the 6,7-, 8,9-, 9,10-. and 11,12-members of the high and low melting series were obtained on a Perkin-Elmer Model 21 instrument by using the scanning and sampling techniques described. Some of the potassium bromide pellets were foggy and caused excessive scattering. Increasing the pressing time from 5 to 10 minutes eliminated this difficulty. Prolonged grinding (up to 10 minutes) was also tried, but resulted in loss of detail in the resulting spectra, probably because of a breakdown of crystallinity. Polymorphism is not ruled out in the dihydroxy acids, although care was taken to prepare all the samples by identical procedures (9).

Results and Discussion. All hydroxylated acids show strong absorption around 3400 cm.$^{-1}$ and a series of medium strength bands between 1000 and 1200 cm.$^{-1}$, corresponding to the O—H stretching vibrations and the C—O— stretching and/or deformation vibrations, respectively. The 1180- to 1350-cm.$^{-1}$ region shows only weak bands with no apparent regularity.

The infrared spectra are extremely similar above 1550 cm.$^{-1}$, showing a broad, unresolved O—H band around 3400 cm.$^{-1}$, C—H stretching bands around 2900 cm.$^{-1}$ and the carboxyl band at 1710 cm.$^{-1}$ Figure 5 gives the observed spectra in the 700- to 1550-cm.$^{-1}$ region. The most obvious differences between the various isomers occur between 1000 and 1150 cm.$^{-1}$,

in a region commonly associated with COH vibrations. Members of the high melting series are clearly distinguishable from the corresponding low melting substances by a comparison of the absorption patterns in this region. The low melting members have a more complex structure, as might be expected from the complicated interactions and hydrogen bonds, which are possible if both groups are on the same side of the chain. (Similar complexities might be expected in the OH stretching region if investigated under higher resolution. Current studies with sodium chloride optics showed merely the presence of a broad unresolved band which was similar for all compounds.) The differences between the individual members within one series are small, but sufficient to allow identification and differentiation in a number of instances. No regularities comparable with the band progression of unsaturated acids could be detected.

Aside from the bands which could be associated with the hydroxyl groups, puzzling phenomena appear on bands commonly associated with the carboxyl group. Thus, the strong band usually appearing around 1300 cm.$^{-1}$ is occasionally shifted to 1225 cm.$^{-1}$ and the band around 925 cm.$^{-1}$ is split into a number of weaker bands, giving rise to a pattern which appears to be different for each compound. Together with the 1000- to 1200-cm.$^{-1}$ region this furnishes sufficiently distinctive fingerprint patterns to allow the identification of each individual isomer by infrared spectra.

The position isomers of contiguously substituted dihydroxystearic acid could not be identified by clear-cut regularities like the *trans*-monounsaturated acids, but in the region roughly between 800 and 1200 cm.$^{-1}$, there is enough spectral detail to allow identification on a fingerprint basis.

ACKNOWLEDGMENT

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